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13. ABSTRACT (Maximum 200 words) Positronium decay was used to measure pore size distribution in porous sol-gel glass. It was also used to determine the population of surface strained rings at various stages of firing and drying procedures. Rotational and translational diffusion of molecular liquids, semiconductor clusters, and fullerenes was investigated. Preferential adsorption, surface interactions and their effects on electronic transitions, vibrational relaxation, rotational and translational motion were discussed. Computer simulations for molecular motion of SF <sub>6</sub> and cyclohexane inside small pores were run as a function of temperature and pressure. Results were compared with experimental data. Experimental evidence for the pentavalent transitions state for TMOS and TEOS hydrolysis reactions were provided.					
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# HYDROLYSIS REACTION AND POSITRONIUM DECAY IN SILICA GELS

AFOSR-90-0165

## FINAL TECHNICAL REPORT

The research program supported by the AFOSR can be divided into three projects:

1. Positronium Decay in Silica Gels
2. Reorientational and Translational Motion of Molecules Inside Porous Silica.
3. Hydrolysis reaction of TMOS

Each project is discussed separately and is followed by a list of publications.

### 1. Positronium decay

#### *Pore size distribution*

We showed that positronium lifetime in porous silica gels depends on pore diameters and we proposed to estimate a possibility of using positronium decay technique to determine pore size distribution in sol-gel glass. All experiments were conducted under vacuum condition. A computer program was written and tested for a mixture of two silica samples of distinctly different pore diameters. Time decay spectrum of the mixture was numerically separated into two components, and the analysis showed that pore diameters and total pore volume of each component were in agreement with the BET data.

Much accurate results were obtained by using CONTIN, a program developed by Provencher and later modified by Gregory. Positronium decay spectra were separated into

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components, each corresponding to different pore diameters. Relative intensities of each of the components were used to estimate the pore size distribution. The program was tested for different mixtures of silica powders, each of narrow distribution of pore diameters.

This study showed that positronium decay can provide information not only on the average pore diameter but also on the pore size distribution. At the present time, however, this method can be used only in a laboratory environment, and further studies are necessary to be able to extend the use of this method to field applications. This is caused by the dependence of positronium lifetimes on quenching properties of surface groups and molecular species present inside the pores. Therefore, to use the positronium decay technique for the analysis of pore size distribution it is necessary to run separate calibration runs for different surface groups and molecular gases present inside the pores.

#### *Positronium quenching by adsorbents and surface groups*

The experiments described below were run to provide information on positronium decay in porous silica under different atmospheric and surface conditions. We investigated the quenching effect of molecular oxygen, nitrogen, and carbon dioxide on positronium in silica gels. We found that at room temperature about one oxygen molecule per pore can effectively quench positronium, but liquid oxygen adsorbed on pore surfaces is less reactive. At 77 K more than 400 oxygen molecules have to be present in an average pore to reduce positronium lifetimes to a similar degree as one oxygen molecule in a gaseous state at 300 K. The cross section of positronium quenching due to a monolayer of adsorbed oxygen at 77 K was calculated and was found to be at least two orders of magnitude smaller than the cross section for conversion quenching by subsequent layers, and was similar to that observed in gaseous oxygen, the so-called pick-off process. The cross section for the subsequent layers was typical for the converging quenching. No evidence was found to indicate that an excited O<sub>2</sub>-positronium complex formation leads to chemical quenching.

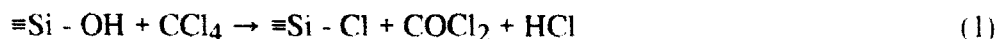
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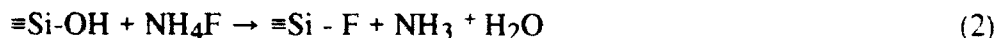
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We also showed that nitrogen and carbon dioxide reduce slightly decay lifetimes due to the pick-off process. But no differences in the cross sections were observed between the gaseous and liquid phases.

Another study was conducted to find the effect of different surface groups on positronium lifetimes. We developed various techniques to replace hydroxyl groups with different atoms, and we found that the most effective was chlorination reaction



which is carried in vacuum, at 500°C and results in more than 95% of hydroxyl groups being replaced by chlorine atoms. The procedure is discussed in Ref. 6. Other methods, such as fluoridation



methoxylation, iodination, or treatment in HMDS also were found to be effective. It is important to note that samples remained transparent after treatments. Although the hydroxyl groups were found to be slightly more effective quenchers than groups such as  $\equiv\text{Si} - \text{Cl}$ ,  $\equiv\text{Si} - \text{CH}_3$  or  $\equiv\text{Si} - \text{F}$ , in general, surface modification did not cause significant changes in the observed lifetimes.

#### *Strained surface rings*

Water adsorbed on the surface causes rehydration of a fully dehydroxylated surface, and this process can be probed by Raman scattering and by positronium decay. Raman spectroscopy has been used before by Brinker, Hench and others to study surface groups. The Raman bands labeled D<sub>1</sub> and D<sub>2</sub> are believed to correspond to 4 and 3 member surface rings, respectively. We showed that although Raman studies can provide qualitative information on the changes in the population of the strained rings, Raman cannot

be used to determine their surface densities. However, this information can be provided by positronium decay studies.

Positronium lifetime in porous silica depends on the amount of adsorbed water. Since water reduces the surface density of strained rings this result indicates that the strained rings are very effective quenching sites. (A product of the hydrolysis reaction, silanol groups, can also quench positronium, but they are not effective quenchers. Furthermore, we also showed that small concentrations of water adsorbed on pore surfaces of gels dried at temperatures of less than 200°C behave inertly with respect to positronium.) From the amount of adsorbed water corresponding to the maximum lifetime, the total surface area of the pores, and from the molecular size of H<sub>2</sub>O molecule, we estimated the surface density of the strained rings. The surface population of the strained rings increases with temperature as

$$N(T) = 0.08 \exp (0.00423 \cdot T) \quad (3)$$

where T is temperature in degrees Celsius. The parameters in the above equation are accurate within 25%. For example, we estimate surface densities of strained rings for a sol-gel fired at 770°C to be 2.1 rings/nm<sup>2</sup>. This calculation of surface ring density is in a very good agreement with the 20 to 40% coverage estimated from the analysis of NMR spectra and the surface coverage of silicon atoms (Brinker). It also agrees with the findings of computer simulations of porous silica structure by Garofallini, who estimated that there are 2 to 4 three member rings per nm<sup>2</sup>.

The above formula has been derived assuming that pore diameters do not change with the firing temperature. This assumption is true for the manufacturing technique developed by Hench et al., but may not be valid for other drying and firing schedules. This equation may be used for temperatures up to 950°C, above which pore narrowing and pore collapse have been observed. The details are presented in Ref. 16.

In an independent study, strained rings were shown to be strong adsorption sites for ammonia. Raman investigations on Fermi resonance in ammonia adsorbed on silica showed that ammonia is adsorbed more readily on surface rings than on hydroxyl groups. The results are discussed in Ref. 15. This finding was later confirmed by positronium decay investigation, Ref. 16. For small concentration of ammonia, positronium annihilation rates are systematically higher for  $\text{NH}_3$  adsorbed on OH groups and strained rings, as opposed to fluorine sites of the treated samples. We explained this finding in terms of ammonia-surface interactions. Upon adsorption on strained rings or hydroxyl groups ammonia undergoes deformations, the bond lengths shorten and the bond angles are distorted, and in result positronium is quenched more effectively than by a free ammonia. The charge redistribution in ammonia adsorbed on a three member ring is more pronounced than for ammonia adsorbed on silanols. These results were confirmed by AM1 calculations conducted by Dr. J. West.

## **2. Reorientational and Translational Motion of Molecules Inside Porous Silica**

Understanding of diffusion and adsorption of liquids on porous materials is essential for explaining the separation of solutions, mechanics of flow through small pores, heterogeneous catalysis, optical properties of impregnated porous glass, and others. Porous silica sol-gel glass stabilized at 700°C (or at higher temperatures) represents an interesting material for studies of surface interactions and molecular motion in restricted geometries. Sol-gel glass samples are transparent, pore diameters can be controlled over a wide range (12 Å to 200 Å), and surface interactions can be modified by replacing hydroxyl groups with other functional groups. Pore diffusion differs from ordinary molecular diffusion in gases and liquids because it is heavily influenced by the pore structure and surface interactions. The pore surface of sol-gel glass is covered with

silanols and strained rings, and these groups can interact with adsorbed molecules. These interactions may determine molecular motion within the pores or at least in the proximity of the pore walls. As discussed before (Eqs. 1-2) we modified surface interactions by replacing Si-OH groups with other less active bonds such as Si-OCH<sub>3</sub>, Si-Cl, Si-F, or S-(CH<sub>3</sub>)<sub>3</sub>. The effect of modified surfaces on dynamics of adsorbed species was investigated for ammonia, methyl iodide, CHCl<sub>3</sub>, CS<sub>2</sub>, SF<sub>6</sub>, pyridine, acetone, cyclohexane, and acetonitrile inside small pores.

#### *Vibrational relaxation*

Methyl iodide was selected for these experiments because there is an extensive literature on vibrational and reorientational relaxation in the pure liquid phase and in various solvents. These investigations established that vibrational relaxation of the  $\nu_1$  band is due to energy dissipation processes, while the  $\nu_2$  and  $\nu_3$  bands are broadened by intermolecular resonance energy transfer and vibrational dephasing caused by fluctuations in intermolecular potential. All these very different vibrational relaxation processes were affected by surface interactions which include hydrogen bonding with silanols and interactions with strained rings. These interactions are also important for liquids that usually are assumed to be inert solvents. This is an important finding in view of numerous attempts to use sol-gel glass as a host material for impregnation.

For carbon disulfide in the bulk phase and inside porous sol-gel glass no changes in vibrational relaxation have been detected. But for the C-H stretching modes of chloroform and acetonitrile we observed faster relaxation in porous silica, including samples of modified surfaces. For decreasing pore diameter, the surface-to-volume ratio increases and most of the molecules trapped within the pores find themselves in a close proximity of the surface, and surface interactions perturb intermolecular potential of adsorbed molecules.

### *Fermi resonance*

Fermi resonance between two vibrational molecular modes is very sensitive to intermolecular interactions. Fermi resonance in adsorbed molecules is perturbed by surface interactions, and thus it can provide information on adsorbent-adsorbate interactions. Fermi resonance is responsible for the energy transfer from one mode to another, which results in intensity shift between the two components of the doublet in resonance. For example, we observed that for a small amount of ammonia adsorbed on silica one component is much more intense than the other, but for the pores completely filled with ammonia both bands are equally intense. From experimental band shapes of ammonia adsorbed on silica we calculated the frequencies of uncoupled modes and the Fermi coupling parameter. These values were obtained for different surface coverage and for silica of untreated and fluorinated (Eq. 2) surfaces. No evidence of hydrogen bonding between ammonia and fluorinated surfaces has been detected. However, Fermi resonance was found to be perturbed to a greater extent by the fluorinated surface than by the hydroxylated samples. We explained this effect in terms of strong interactions between ammonia and strained surface rings (compare section on positronium decay). In the non treated samples, ammonia is adsorbed both on strained rings and hydroxyl groups, while in fluorinated samples only on strained rings. Hydroxyl sites were found to be energetically weaker. Similar results were obtained for acetonitrile adsorbed on porous silica.

### *Preferential adsorption*

Acetone and pyridine form strong hydrogen bonding with hydroxyl groups on the pore surfaces and thus their spectra undergo dramatic changes. We used this property to estimate the population density of OH groups on the pore surface as a function of temperature at which the samples were treated. It varies from 5 OH groups per nm<sup>2</sup> for samples dried at 180°C to 1.5 for samples fired at 800°C. These results agree well with



the IR studies. We showed that the Raman technique used to estimate the population of hydroxyl groups is almost as sensitive as the IR method. Due to large surface area of porous sol-gel glass, small amounts of adsorbents equivalent to 0.5% surface coverage can be easily detected. The experiments can be done in situ and no special preparation is required. Moreover, this is a nondestructive technique and can be used during the production process.

We observed that pyridine is preferentially adsorbed on silica and this process results in a bilayer structure of the interface. The bilayer structure was observed even at the lowest concentration of pyridine in the sample. Instead of forming a single layer, pyridine adsorbed onto the surface in the form of a double layer. The top layer is attracted by electrostatic charges accumulated by the bottom layer. When pyridine was dissolved in a solvent and this solution was used to impregnate a sol-gel, pyridine also formed a binary layer which resulted in an increased concentration of that liquid inside the pores. The increased concentration of pyridine in porous silica sol-gel was observed in binary mixtures with acetone, chloroform, carbon tetrachloride, nitromethane, and carbon disulfide. For example, for CS<sub>2</sub> solutions in small pores, diameter 28 Å, the concentration of pyridine inside the pores was three times greater than in the liquid outside of the sample. Preferential adsorption was also observed in other polar liquids, such as acetonitrile or acetone. This study indicated that one has to be very careful when impregnating porous materials since the concentration in the pores may be very different from that of the parent solution. This problem is of primary importance in doping glass with index of refraction modifying materials, manufacturing sol-gels impregnated with dye lasers, and in other applications.

#### *Rotational and translational diffusion*

Translational and rotational motions of molecules inside the pores are slowed down due to two different effects, surface interactions and geometrical restrictions. In order to

separate the two effects we used samples of various diameters and of modified surfaces. Diffusion coefficient was experimentally determined for pyridine and acetonitrile, compare Refs. 8, 9. Rotational motion of molecules adsorbed in the pores was studied for chloroform, sulfur hexafluoride, acetonitrile, and acetone. Hydrogen bonding plays a dominating role in slowing molecular reorientation especially in the first monolayer, where molecules undergo librational type of motion with large initial angular jumps. When there is no hydrogen-bonding interaction between the adsorbed molecules and the surface, the molecular reorientational relaxation is only slightly depended upon pore diameter. This conclusion is based on the observation of reorientational motion of  $\text{SF}_6$ ,  $\text{CS}_2$  and nitromethane, the molecules that do not form H bonds with hydroxyl groups.

Our study on reorientational motion of  $\text{SF}_6$  was the first experimental work under high pressure done for molecules imbedded inside the pores. We observed a dependence of the rotational relaxation time on both temperature and pressure, and compared the results with two models for rotational motion, the extended diffusion theory and the Fokker-Planck frictional model. Both models have different foundations, but they lead to similar results, collisions with the walls are less effective in changing the angular momentum than intermolecular collisions. To provide more information on molecular motion of  $\text{SF}_6$  in small geometries we decided to run molecular dynamics computer simulations.

#### *Molecular dynamics computer simulations*

In molecular dynamics computations  $\text{SF}_6$  was represented by a set of (12-6) L-J potentials. In order to determine the potential parameters we ran a series of simulations for the pure system as a function of temperature and pressure, compare Ref. 14. It is not only the molecules inside the pores, but also the structure of the pore that needed to be modeled. We considered pores of different shapes, including a cylindrical pore, a chain of spherical cavities, and a cavity formed by silica clusters placed at the corners of a cube. Results were similar and we decided to concentrate on one model only, namely, the cylindrical pore.

This model was created in a following way. First, the structure of amorphous silica was obtained by melting the cristobalite structure at a temperature above the melting point, and then slowly decreasing the temperature to 296 K. The potential between the atoms constituting silica was assumed to be two body potential in the form

$$U = \sum_i \sum_{j < i} \left[ A_{ij} \exp \left( -\frac{r_{ij}}{\rho} \right) + \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} \operatorname{erfc} \left( \frac{r_{ij}}{\beta_{ij}} \right) \right] \quad (4)$$

where  $r_{ij}$  is the distance between  $i^{\text{th}}$  and  $j^{\text{th}}$  atoms,  $Z_i$  is the electrostatic charge, and  $A_{ij}$ ,  $\rho$  and  $\beta$  are potential parameters. Due to thermal fluctuations the positions of silicon and oxygen atoms were varying in the vicinity of the equilibrium positions, but as the temperature was decreased, their positions were "frozen" at random locations, resulting in different bond lengths and angles between the bonds. The final structure of the amorphous silica was represented by a cube of size of about 58 Å, and containing 12,288 atoms. This cube was obtained by simulating a set of 192 silicon and oxygen atoms, and repeating the equilibrium structure four times along the x,y and z axes.

In the next step, we created pores inside the cube by removing some of the silicon and oxygen atoms. Most of the oxygen atoms found on the surface of the pores formed bridges between adjacent silicons, but we also found a significant number of non-bridging oxygens. We assumed that these non-bridging oxygens represented hydroxyl groups. A random removal of atoms may result in less than tetravalent coordination of some of silicon atoms. To avoid this nonphysical result, the surface structure was corrected by removing these atoms. This procedure resulted in an increased number of hydroxyl groups represented by non-bridging oxygens. Approximating the pore surface by the surface of an ideal cylinder, we found the upper limit of the concentration of the hydroxyl groups (non-bridging oxygens) to be 7.9 per nm<sup>2</sup>. This value matches available data on the surface density of silanols for gels dried at 115°C.

When SF<sub>6</sub> molecules were placed inside the pores, their motion was determined by interactions with other molecules and silica framework. From the resultant intermolecular potential we calculated forces exerted on individual molecules. The Newtonian equations of motion were solved using Verlet's algorithm with time step of 0.005 ps, whereas the orientations of the molecules were computed from eulerian rigid body equations using the forth order predictor-corrector technique. The molecules were placed randomly inside the pores, allowed to interact between themselves and the pore walls, and after equilibrium had been reached, the orientation and angular velocity of each molecule were recorded at time intervals 0.04 ps. Simulations were run for the same temperature and conditions as Raman scattering measurements. We calculated the radial density distribution, angular and linear velocity correlation functions, mean square displacement (diffusion coefficient), rotational correlation function and reorientational correlation times were obtained. A good agreement between experimental and theoretical correlation functions was obtained only when we assumed that the actual density of adsorbed fluid inside the pores was less than the density of the bulk material under the same conditions. This results was the first indication that the filling factor in pores may be less than the value estimated solely from the total volume of the pores.

The simulations were extended to cyclohexane. Potential parameters for cyclohexane in the form of the six-center L-J model were determined by fitting latent heat of evaporation, the configurational energy along the saturated vapor curve, and the diffusion coefficient in the pure liquid phase with available experimental data. Structural and dynamic properties of cyclohexane in the pure phase and in the pores we computed as a function of temperature. In the pure phase the melting point was observed at about 6°C, in excellent agreement with the observed value. As expected translational diffusion coefficient was reduced by a couple orders of magnitude when temperature dropped below the melting point. However, rotational diffusion was practically unchanged in the solid phase indicating that this is a plastic crystal. Computer simulations of cyclohexane in porous

silica were carried out for a wide range of pore diameters, different pore geometries (spherical, cylindrical, irregular shapes), temperatures from  $+100^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$ , and various surface potentials. In porous silica the melting transition of cyclohexane was always observed at lower temperatures. The temperature of the liquid-solid phase transition appears to depend on the pore diameter. For example, for the 20 Å pore the melting transition was lowered by more than  $40^{\circ}\text{C}$ . Simulations were also run at a constant temperature and we varied the pressure inside the pores. At room temperature, the simulated melting point in the pure system was observed at 700 bar, in agreement with the experimental values. In the pores, depending on their diameters, the liquid-solid phase transition was also shifted, and was observed at 3.5 kbar for a 50 Å pore, and over 4 kbar for a 30 Å pore.

Another important observation made during the simulations of cyclohexane in the pores was related to the two-dimensional like motion of the monolayer of cyclohexane on the pore surface. The thickness of this layer is about 5 Å. During the time of simulations, 50 ps, cyclohexane molecules did not leave the surface layer, and their motion can be treated as a 2-D motion. This means that the surface potential plays a crucial role in determining dynamics of molecules in the pores. Similar results have been obtained for translational diffusion, again near the center of the pore molecules can move faster than near the pore walls. Simulations run for  $\text{SF}_6$  or cyclohexane in the pores of various diameters and at different temperature and pressure conditions supported our previous conclusions based on experimental work, that rotational relaxation is dominated by surface interactions.

#### *Semiconducting clusters*

Other projects carried out included experimental studies on photoluminescence of semiconductor clusters and on diffusion of fullerenes in porous silica. Transparent and monolithic sol-gel glass samples stabilized at  $750^{\circ}\text{C}$ , and of the average pore diameter of

35 Å were impregnated with an ethylpyridine solution of CdSe clusters of average diameter 30 Å. This was the first successful impregnation of porous sol-gel glass by the diffusion technique. After drying and heat treatment up to 200°C samples were characterized by both absorption and photoluminescence spectroscopy. After the treatment, the materials were stable, and their optical properties have not changed over a couple of months time period. Due to preferential adsorption glasses can be doped with a higher concentration of CdSe clusters on a per volume basis than present in the parent cluster solution. compare the section on preferential adsorption. The effect of different functional groups present in the sol-gel pores, Cl<sup>-</sup> versus OH<sup>-</sup>, on the properties of the diffused CdSe was reported in Ref. 12. We found that cluster emission properties are ultimately related to the surface composition of the host material, confirming the fact that the observed CdSe photoluminescence is related to cluster surface defects rather than to a bulk excitonic mechanism.

A study on diffusion of fullerenes in porous silica has been recently completed (a paper has been submitted for publication), and we showed that the diffusion coefficient of fullerenes is about 4 times slower than the diffusion coefficient of the carrier, toluene or cyclohexane. By diffusing C<sub>70</sub> dissolved in toluene we successfully produced a concentration gradient of the fullerene inside porous sol-gel glass (paper in preparation). This result indicated that it is possible to produce a GRIN glass by the diffusion method.

In another attempt we tried to produce a Kerr cell. The goal of this study was to impregnate porous sol-gel glass with a polar liquid, such as nitrobenzene, and by applying a strong electric field generate an optically active material to be used as a fast switch. Unfortunately, all our attempts failed, due to difficulties with producing sol-gel glass free of stress induced birefringence.

### 3. Hydrolysis reaction

The aim of this study was to characterize the mechanism of the hydrolysis reaction of silicon alkoxides. High pressure Raman spectroscopy was used to monitor the hydrolysis reaction of TMOS and TEOS in solutions with methanol, acetonitrile, acetone, dioxane, and formamide. The rate constants were experimentally determined from the band intensities for temperatures between 6°C and 60°C, and pressures varying between 1 and 2000 bars. The effect of pH of water was studied in the pH range between 2.0 and 6.0. We found that the rate of hydrolysis reaction depends on the alkoxide used, the properties of the solvent added, and the pH of water. These experimental rates were fitted to the Asano function to determine the volume of activation. The volume of activation, was practically independent of the solvent, the relative concentration of water, the pH and the alkoxide, and equal about  $-40 \text{ cm}^3/\text{mole}$ . Volume of activation can be separated into two components, one which is due to the change in the volume of the solvation, and another due to the change in the volume of the solute. The effects of electrostatic interactions, viscosity, and hydrogen bonding on the reaction mechanism and both components of the volume of activation were evaluated, and a mechanism involving a hydrogen bonded intermediate that contains five-coordinate silicon was proposed. The intermediate state is a pentacoordinate state that forms a strong quadrupole moment. The geometry of the transition state can be approximated by a deformed trigonal bipyramid in which the donor site occupies an axial site. Three methoxy sites are in equatorial sites, and the forth group is opposite to the hydroxyl. Axial bonds are longer than equatorial bonds, and consequently they are weaker, and the methoxy groups opposite the attacking hydroxyl group will leave the system. When a molecule capable of forming a strong hydrogen bond, such as a formamide, is coupled to an Si-OR group, this interaction weakens the Si-O bond by shifting the electron cloud toward formamide, thus enabling more pronounced changes in bond lengths and angles that are necessary to accommodate the additional bond in the

transition state. By protonating the  $\text{OCH}_3$  group the hydrogen bond interaction accelerates the reaction. The details of this research are presented in Refs. 1 and 2.

### **List of Students Participating in the Project**

The following doctoral graduate students had been working on the project: Guen Hoang, Brian Hopkins, Leseq Nikiel, Jeffrey Watson, Neil Koone, and Yong Shao. G. Hoang graduated in 1990, L. Nikiel in 1991, J. Watson in 1991, and B. Hopkins in June 1992. Yong Shao and Neil Koone currently work on studying the diffusion mechanism of the molecules and metal cations in porous sol-gel glass. Five undergraduates students, Mike Crane, Mike Hall, Brian Alvey, Lynette Kugler, and Greg Beauchamps have been involved in the various stages of the project on a part time basis. One post doctoral associate, Dr. Alexander Brodka, worked on computer simulations, another, Dr. B. Hopkins, on positronium decay.



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